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Negative Adsorption of Anions by Suspensions of Bentonites

Attention has been drawn to the negative adsorption of anions of sodium salts by MATTSON[1], SCHOFIELD[2], and BOLT[3]. We have carried out similar measurements, using a somewhat different experimental technique: the anions, of which the adsorption was measured, were $I^*O_3^-$ and $Cr^*O_4^{--}$, where I* and Cr* indicate the radioactive isotopes.

Isotope	Activity	$\tau_{1/2}$
I 131	β^-, γ	8·04 *d*
Cr 51	EC, γ	27·8 *d*

The already purified Wyoming bentonite, which was most kindly put at our disposal by Dr. J. W. JORDAN, Director of the Baroid Division of the National Lead Company, Houston, U.S.A., was kept in suspension for 3 weeks; it was then centrifugated, in order to eliminate the finest fraction; the centrifugated fraction was brought into suspension (about 1 g/100 cm³); to this suspension were added the radioactive tracer (in concentrations of some μ moles/l) and the electrolyte which we wanted to study for its influence on the adsorption of $Cr^*O_4^{--}$ or $I^*O_3^-$. The volume of suspension was stirred, then centrifugated, and the γ-activity of the supernatant liquid measured by a well-type crystal.

The most clear-cut results were obtained with Na-bentonite + NaCl and Ca-bentonite + $CaCl_2$; more intricate were the results obtained with H-bentonite + HCl, where the adsorption turned out to be strongly time-dependant.

The phenomenon of negative adsorption is most readily explained by the assumption that a certain volume of water is inaccessible for anions, due to electrostatic repulsion (the value of ζ must be considerable).

We expected that the addition of electrolyte would destroy this inaccessibility; this expectation was fulfilled. Two causes can be conceived:

(1) The layer where the electric repulsion is effective becomes very thin (pushing in of the double layer—SCHOFIELD—); then the formulae of the double layer must be applied.

(2) The inaccessible volume is constituted by water between the ionic layers of the bentonite; this water is pushed out of the bentonite when the electrolyte concentration in the intermicellar water is increased. If this is the correct explanation, the viscosity of the suspension must change strongly together with the change in the negative anion adsorption.

Measurements of the viscosity brought to light only very small viscosity changes; hence the SCHOFIELD explanation is confirmed.

We then compared the two tracers $Cr^*O_4^{--}$ and $I^*O_3^-$; we studied the following systems:

(a) Na-bentonite + NaCl (0·001 N, 0·002 N, 0·005 N, and 0·01 N), tracer NaI^*O_3,

(b) Na-bentonite + NaCl (same concentrations), tracer $Na_2Cr^*O_4$,

(c) Na-bentonite + Na_2SO_4 (same concentrations), tracer $Na_2Cr^*O_4$,

(d) Ca-bentonite + $CaCl_2$ (0·0001 N, 0·0002 N, 0·0005 N, and 0·001 N), tracer NaI^*O_3.

The results shown in Table I can be expressed as follows:

(1) The difference between the adsorption of NaI^*O_3 and $Na_2Cr^*O_4$ is only slight.

(2) There is practically no difference between the influence exercised by NaCl and Na_2SO_4.

(3) The effects exercised by $CaCl_2$ are comparable to those exercised by NaCl if the normality of $CaCl_2$ is 10 times, the concentration in moles/l 20 times smaller than the corresponding quantities for NaCl.

Interpretation of results.—We shall use the simplified picture, that a layer of thickness δ is inaccessible to the anions; now, if g grams of bentonite are suspended in a volume V, if s is the specific surface area of bentonite, we have for the change in anionic concentration

$$\frac{\Delta c_-}{c_-} = \frac{\Delta V}{V} = \frac{gs\delta}{V}. \tag{1}$$

On the other hand, if Γ^- is the negative adsorption per cm²:

$$gs\,\Gamma_- = V\Delta c_-. \tag{2}$$

Hence

$$s\delta = \frac{V\Delta c_-}{g^- c} = \frac{s\Gamma_-}{c_-}. \tag{3}$$

For δ we can insert the value following from the Debye-Hückel theory

$$\delta = \varkappa^{-1} = \sqrt{\frac{DRT}{4\,\pi\,F^2}}\,\frac{1}{\sqrt{\Sigma \nu_k z_k^2}}\,\frac{1}{\sqrt{c}}. \tag{4}$$

Thus, however, we cannot explain the factor 20 between the concentrations of NaCl and concentrations of $CaCl_2$; equation (4) would provide us only with a factor 3, hence the double layer theory must be applied in the form which does not contain the Debye-Hückel approximation; thus we arrive at the conclusion that $\zeta \gg RT/F$ (25 mV).

For δ can we also insert the value following from the non-approximated double layer theory, valid for a z-z-valent electrolyte (since NaCl and Na_2SO_4 gave concordant results, no distinction need be made between a 1-1-valent and a 1-2-valent added electrolyte, nor between a 2-1- and a 2-2-valent one).

$$\frac{d\psi}{dx} = \frac{\zeta}{\delta} = \frac{RT}{F}\sqrt{\frac{8\,\pi\,F^2}{DRT}}\left[e^{-\frac{\zeta}{2RT/zF}} - e^{\frac{\zeta}{2RT/zF}}\right]\sqrt{c}. \tag{5}$$

In this expression we shall neglect the last of the two exponentials, hence

$$\delta \simeq \frac{\zeta}{RT/F}\sqrt{\frac{DRT}{8\,\pi\,F^2}}\,e^{\frac{\zeta}{2RT/zF}}\,\frac{1}{\sqrt{c}} \tag{6}$$

where c is the concentration in moles/cm³.

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[2] R. K. SCHOFIELD, Nature *2*, 408 (1947).

[3] G. H. BOLT, Kolloid-Z. *1*, 41 (1958).

Table I.
Negative anion adsorption ($\Delta c_{-}/c_{-}$ expressed in %) in Na-bentonite and in Ca-bentonite, as a function of the concentration of added NaCl, Na_2SO_4, and $CaCl_2$

Tracer	Bentonite	Electrolyte	Normality						
			0·0001	0·0002	0·0005	0·001	0·002	0·005	0·01
$NaI^{*}O_3$	Na-bentonite	NaCl	—	—	—	+5·36	+4·7	+3·29	−2·3
	Ca-bentonite	$CaCl_2$	+5·74	+4·51	+3·53	+2·32	—	—	—
$Na_2Cr^{*}O_4$	Na-bentonite	NaCl	—	—	—	+7·02	+6.36	+4,9	+3·9
		Na_2SO_4	—	—	—	+7·04	+5·38	+4·16	+3·65

Now, RT/F is equal to 25 mV; if ζ is also expressed in mV, we may write:

$$\delta = \frac{\zeta}{25} e^{\frac{\zeta}{50/z}} \sqrt{\frac{DRT}{8\pi F^2}} \frac{1}{\sqrt{c}}. \tag{7}$$

In the following equation, we shall assume that the added electrolyte decreases the value of δ, but does not change the value of ζ.

Then equation (7) gives the following result for the ratio of the concentrations of a 1-1- and a 2-2-valent electrolyte leading to the same δ-values:

$$\sqrt{\frac{c_{\mathrm{I}}}{c_{\mathrm{II}}}} = e^{\frac{\zeta}{50}} e^{-\frac{\zeta}{25}} = e^{-\frac{\zeta}{50}};$$

$$\frac{c_{\mathrm{I}}}{c_{\mathrm{II}}} = 20 = e^{-\frac{\zeta}{25}}; \quad \zeta = -75\,\mathrm{mV}.$$

If this value of ξ is introduced into equations (7) and (3) we get

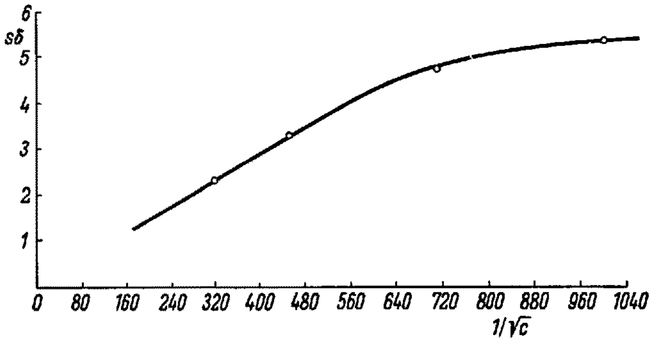
$$s\delta = 3e^{-1,5z}\, s \sqrt{\frac{DRT}{8\pi F^2}} \frac{1}{\sqrt{c}}. \tag{8}$$

We have plotted $s\delta$ as a function of $1/\sqrt{c}$; the curve obtained for a I-I-valent electrolyte, if considered as a straight line, has a slope of $7 \cdot 1 \times 10^{-3}$ cm³/g (Moles/cm³)½.

With $$\sqrt{\frac{DRT}{8\pi F^2}} = 9 \cdot 6 \times 10^{-10}\ c\,g\,s.,$$

this value of the slope yields

$$s = 1110\ \mathrm{m^2/g}.$$



We have also plotted $s\delta$ as a function of $1/\sqrt{c}$ for a 2-2-valent electrolyte; the straight line obtained did not pass through the origin; therefore we could not calculate the value of s from these results.

Let us finally mention that we also studied the adsorption of $NaI^{*}O_3$ by H-bentonite to which amounts of HCl were added; here however the results turned out to depend strongly on time; an initially negative adsorption changed into a positive adsorption; an initially weak positive adsorption changed into a more and more strongly pronounced positive adsorption, as may be seen from Table II.

Table II.
Time dependance of negative anion adsorption by H-bentonite

Bentonite	HCl	immediately	3 h	6 h	1 day	3 days	6 days	10 days	20 days
H-bentonite	0	+6	+ 5·5	+ 5·2	+ 3·5	+ 4	+ 3·3	+ 0·9	+ 0·6
	0·001 *N*	+ 2,6	+ 1·7	+ 0·8	− 1·3	− 1·3	− 3	− 6·1	− 6·8
	0·01 *N*	− 2·6	− 5·4	− 6		−11·5	−18·6	−20·2	−33·3
	0·1 *N*	−24·9	−50·2	−57·2	−69·6	−53	−47·8	−44	−58
Bentonite	**NaCl**	**immediately**	**3 h**	**6 h**	**1 day**	**3 days**	**6 days**	**10 days**	**20 days**
Na-bentonite	0	+ 7·9	+ 8·2	+ 9·1	+ 9·2	+ 8·1	+ 7·9	+ 7·9	+ 7·5
	0·001 *N*	+ 6·1	+ 6·8	+ 6·3	+ 7·2	+ 6·4	+ 5·6	+ 5·3	+ 6·2
	0·01 *N*	+ 1·7	+ 1·7	+ 2·6	+ 1·1	+ 1·7	+ 1·2	+ 1·7	+ 0·24

The Na-bentonite did not show a similar effect.

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Laboratory for Physical Chemistry, University of Ghent, May 6, 1958.

Résumé

Nous avons étudié l'adsorption négative des anions $I^*O_3^-$ et $Cr^*O_4^{--}$ à différents bentonites en fonction d'électrolytes additionnés. Pour les électrolytes NaCl et Na_2SO_4 les résultats sont en bon accord avec ceux de Schofield et Mattson; nous avons étudié aussi l'effet de l'addition de solutions de $CaCl_2$; celles-ci produisent le même effet à des dilutions 20 fois plus grandes que les solutions de NaCl. Comme ceci ne peut pas être expliqué sur la base de la théorie de Debye-Hückel, nous avons appliqué la théorie exacte de la couche double; le facteur 20 mentionné plus haut mène à une valeur de $\zeta = -75$ mV. En introduisant cette valeur de ξ, une représentation graphique $s\delta - 1/\sqrt{c}$ pour les résultats des expériences au Na-bentonite + solutions de NaCl, donne une surface spécifique de 1110 m^2/g.

The Structure of Schmidt's Aluminium Hydroxide Gel

Aluminum hydroxide gels are used as adsorbents for proteins, enzymes, and viruses, particularly for preparing vaccines against foot-and-mouth disease[1]. The gel first used for this purpose was Willstätter's C-gamma gel, which was the final product of aging in aqueous solution of the C-alpha gel, which is amorphous aluminum hydroxide, through an intermediary C-beta gel, which is the aluminum oxide monohydrate, Boehmite[2]. These transformations are slow, taking months for completion into the C-gamma gel. Schmidt[3] modified Willstätter's procedure by autoclaving the C-alpha gel at 120°C in order to obtain a stable product in a shorter time. The gel thus obtained is considered similar to Willstätter's C-gamma gel[4]. The purpose of this communication is to show, by X-ray diffraction and electron microscopy, that Schmidt's gel is made up of particles which are different in crystalline structure, morphology, and dimensions from Willstätter's C-gamma gel, but similar to Willstätter's C-beta gel.

Schmidt's gel was prepared according to the original paper[3], or obtained as sold by Aktieselskabet Kemisk Industri from Kopenhagen[1]. Willstätter's C-gamma gel was prepared by the original procedure[5], or by Kraut's procedure[6] from ammonium alum. The gels were prepared for and examined by X-ray diffraction and electron microscopy as described previously[7]. The data from X-ray diffraction powder photographs are listed in the Table along with data on well crystallized Boehmite[8]. Figures 1 and 2 are electron micrographs of Schmidt's gel. Figure 3*A* is of Willstätter's gel and Figure 3*B* is of Kraut's C-gamma gel.

Fig. 1.—Electron micrograph, ×20000 of Schmidt's aluminum hydroxide gel dried on Formvar from aqueous suspension and shadow cast with chromium at arctan 0·32.

From the Table it is evident that both samples of Schmidt's gels have the most characteristic lines of Boehmite[9] and that the lines are different from those of the C-gamma gel which are composed of a mixture of aluminum oxide trihydrates, Bayerite and Gibbsite[10]. Figures 1 and 2 are of Schmidt's gel, dried on a Formvar substrate and shadow cast with chromium at arctan 0·32 showing typical aggregates of fine particles (*X*) and fibrils (*Y*) at low magnification (×20 000) in Figure 1 and at higher magnification (×62 000) in Figure 2. The fibrils range in diameter from about 50 to 100 A.U., Figure 2*A*. Although they appear to be relatively short (lengths average about 400 to 1000 A.U.), and no long, extended fibrils are observed, they can measure as long as about 0·25 μ. While the major portion of the material appears to be fibrous, there are also crystalline particulates in a wide distribution of diameters as large as 0·5 μ and as small as 200 A.U., Figure 2*B*. Both Figures 1 and 2 contain material which is similar to that observed in C-beta gels formed by aging of C-alpha gels at room temperature[11] in pH's greater than 7·4, or to that observed in C-beta gels formed by boiling concentrated aqueous suspensions of amorphous aluminum hydroxides[12] precipitated from aluminum chloride (or nitrate) by ammonium hydroxide solution.

C-gamma gels are composed of particles of a completely different morphology from Schmidt's gels. This is demon-

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